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(54) Title: NOVEL RHEOLOGY REGULATORS SUCH AS GROUND NATURAL CALCIUM CARBONATES OPTIONALLY TREATED WITH A FATTY ACID OR SALT AND THEIR USE

(54) Titre: NOUVEAUX REGULATEURS DE RHEOLOGIE DU TYPE CARBONATES DE CALCIUM NATURELS BROYES EVENTUELLEMENT TRAITES AVEC UN ACIDE GRAS OU SON SEL ET LEUR APPLICATION

(57) Abstract

The invention concerns the selection of an ultrafine natural calcium carbonate, optionally treated with one or several fatty acids or one or several salts or mixtures thereof, and its use as rheology regulator for polymer compositions. The BET specific surface area according to ISO standard 4652 is 14 to 10 m²/g, and the oil absorption is higher than 16 measured according to the ISO 787-V standard (Rub-out method). The use of said ultrafine calcium carbonate enhances the conditions for mixing the constituents and manufacturing as well as the properties of the end product.

(57) Abrégé

L'invention concerne la sélection d'un carbonate de calcium naturel broyé à une grande finesse, éventuellement traité avec un ou plusieurs acides gras ou un ou plusieurs de leurs sels ou leurs mélanges, et son utilisation comme régulateur de rhéologie pour les compositions polymériques. La surface spécifique est de 14 à 30 m²/g mesurée selon la méthode B.E.T. norme ISO 4652, et la prise d'huile est supérieure à 16 mesurée selon la norme ISO 787-V (Rub-out method). On améliore les conditions du mélange des constituants et de la fabrication, ainsi que les propriétés du produit final.

Rheology regulators such as ground natural calcium carbonates optionally treated with a fatty acid or its salt and their use

The present invention concerns the technical sector of mastics, coatings,
5 adhesives, plastisols or rubbers.

There are known, in the field, polymeric compositions with or without a filler,
for example, silane-terminated polyurethanes which are used as moisture-hardenable
mastics or adhesives.

In the presence of moisture, the terminal silane groups undergo, in a known
10 manner, a hydrolysis and condensation reaction. A stable siloxane network (Si-O-Si)
then forms.

Such products have numerous applications in various industrial fields such as the
transport and building industry.

Ever more sophisticated formulations have therefore been sought, notably of the
15 "single-component" type, and capable of being applied on various substrates posing
problems ever more difficult to solve.

The composition of this type of formulation comprises one or more fillers which
can be one or more calcium carbonates usually described as "fine".

It has been discovered according to the invention that, surprisingly, the selection
20 of an ultra-finely ground natural calcium carbonate, which will be described below, or
this calcium carbonate treated also as described below, makes it possible to achieve an
unequalled set of satisfactory properties for the end product. Notably there can be cited a
good adaptability to adhesion on many types of substrate, such as certain difficult plastics,
including those without a prior primary layer or "primer", a reduction in the necessary
25 amount of polymer (and therefore a reduction in the material cost), or also a notable
reduction in the mixing time (possibly achieving a factor of $\frac{1}{2}$ for each step, which has an
obvious considerable economic importance).

It is still more surprising to note that this remarkable improvement in a set of
properties of the end product does not take place, as persons skilled in the art would
30 logically expect, to the detriment of the final mechanical properties, or properties such as
the resistance to chemical agents or UV radiation or similar properties conventionally
required to such agents.

Polyvinyl chloride (PVC) based plastisol formulations are also known.

It should be stated here that a plastisol designates a suspension of one or more
PVC resins in a liquid plasticizer as well as additives such as mineral fillers, stabilizers,



mineral and/or organic pigments, expansion agents, adhesion promoters, liquefying agents and others.

After thermal gelling, the plastisol takes on the appearance of a more or less flexible compact mass.

5 One of the mineral fillers usually used consists of a synthetic calcium carbonate obtained by chemical means (precipitated calcium carbonate: PCC) such as for example the product Winnofil SPT Premium™ de Zeneca.

According to a first aspect of the invention, there is provided a use of a finely ground natural calcium carbonate having a specific surface area of approximately 14 to 10 30m²/g, which is measured according to the B.E.T. method ISO standard 4652, as a rheology controller.

This natural calcium carbonate is chosen from amongst chalk, calcite, marble, alone or in a mixture, or from amongst these same calcium carbonates treated by means of at least one fatty acid or its salt or a mixture thereof and preferentially by means of 15 stearic acid or its salt such as notably calcium stearate, magnesium stearate, zinc stearate and highly preferentially by means of stearic acid or its calcium salt, all this as described in more detail below.

The rheology regulating product according to the invention is characterised in that it is a natural calcium carbonate, with specific surface area of the order of 14 to 20 30m²/g, preferably 16 to 24m²/g, and highly preferentially of the order of 20m²/g measured according to the ISO standard 4652 B.E.T. method.

This carbonate is optionally treated with at least one fatty acid or its salt or a mixture thereof, said acid being an acid containing 10 to 24 carbon atoms, and more particularly stearic acid or its salt such as notably calcium stearate, magnesium stearate, 25 zinc stearate and highly preferentially by means of stearic acid or its calcium salt, preferably at the rate of 0.01% to 5% by weight and more preferentially 1% to 4% by weight.

It should be noted here that stearic acid means industrial quality stearic acids composed principally of 50% to 70% octadecanoic acid and 30% to 50% hexadecanoic 30 acid.



One original advantage of the product according to the invention is that this product is a calcium carbonate which fulfils a rheology regulating function. This function usually falls to the polymers and additives contained in the polymeric formulation such as for example viscosity depressing agents and the Applicant was surprised to see it fulfilled by an
5 ultra-fine natural mineral filler material type product.

The selected product according to the invention consists of an ultra-finely ground natural calcium carbonate in the presence or not of a dispersing agent and optionally treated with at least one fatty acid or its salt or a mixture thereof.

10

Another of its characteristics lies in its oil absorption which is higher than 16, measured according to ISO standard 787-V (Rub-out method).

A calcium carbonate with specific surface of 19 to 26 m²/g was described in patent EP 0
15 795 588. It is known according to this document as a pigment providing high finish and opacity in the field of paper. This field of application is totally different. Moreover, such a function is totally different from that of a rheology regulating action, and nothing would suggest either the function brought to light by the invention, nor the fact that this novel application could lead to a surprising set of properties having very great economic
20 importance.

The invention also concerns the use, as a rheology regulator for the preparation of mastics or coatings, adhesives, plastisols or rubbers, of these ultra-finely ground natural calcium carbonates, optionally treated by means of at least one fatty acid or its salt
25 notably of calcium, magnesium, zinc or a mixture thereof. This acid, which is an acid containing 10 to 24 carbon atoms, is more particularly stearic acid or its salt such as notably calcium stearate, magnesium stearate, zinc stearate and highly preferentially stearic acid or its calcium salt. The treatment is carried out preferably at the rate of 0.01% to 5% by weight and more preferentially 1% to 4% by weight of at least one fatty acid
30 or its salt or a mixture thereof.

The invention also concerns the use of dispersions or suspensions, in an organic medium, of these calcium carbonates, treated or untreated, as a rheology regulator for the preparation of mastics or coatings, adhesives, plastisols or rubbers.

35

The invention finally concerns polymeric plastisol, mastic or coating, elastomer or rubber compositions containing, as a rheology regulator, said ultra-finely ground natural calcium carbonates, optionally treated by means of at least one fatty acid or its salt or a mixture thereof.



Other characteristics and advantages of the invention will be better understood from a reading of the description and examples which follow. These examples do not represent any limitative aspect whatsoever of the invention.

5

In the examples, the products have the following characteristics:

PRODUCT A:

10 A filler of the prior art, consisting of a chalk type natural calcium carbonate, ground and dried, untreated, with mean grain diameter 0.67 micrometres measured by means of the Sedigraph 5100 from the Micromeritics company, with specific surface 11 m²/g measured according to the ISO standard 4652 B.E.T. method.

PRODUCT B:

15 A rheology regulator according to the invention, consisting of a chalk type natural calcium carbonate, ground and dried, untreated, with mean grain diameter 0.60 micrometres measured by means of the Sedigraph 5100 from the Micromeritics company, with specific surface 19.5 m²/g measured according to the ISO standard 4652 B.E.T. method and with oil absorption equal to 18.75 measured according to ISO standard 787-V
20 (Rub-out method).

PRODUCT C:

25 A rheology regulator according to the invention, consisting of an Urganian calcite type natural calcium carbonate, ground by a wet process and dried, untreated, with mean grain diameter 0.44 micrometres measured by means of the Sedigraph 5100 from the Micromeritics company, with specific surface 16.5 m²/g measured according to the ISO standard 4652 B.E.T. method and with oil absorption equal to 20 measured according to ISO standard 787-V (Rub-out method).

30 PRODUCT D:

A rheology regulator according to the invention, consisting of a chalk type natural calcium carbonate, ground by a wet process and dried, treated by the use of 3% by weight of stearic acid, with mean grain diameter 0.59 micrometres measured by means of the Sedigraph 5100 from the Micromeritics company, with specific surface, after treatment,
35 equal to 16 m²/g measured according to the ISO standard 4652 B.E.T. method and with oil absorption, after treatment, equal to 16.3 measured according to ISO standard 787-V (Rub-out method).

PRODUCT E:



A rheology regulator according to the invention, consisting of an Urgonian calcite type natural calcium carbonate, ground by a wet process and dried, untreated, with mean grain diameter 0.58 micrometres measured by means of the Sedigraph 5100 from the Micromeritics company, with specific surface 14.4 m²/g measured according to the ISO standard 4652 B.E.T. method and with oil absorption equal to 17.9 measured according to ISO standard 787-V (Rub-out method).

PRODUCT F:

A rheology regulator according to the invention, consisting of a chalk type natural calcium carbonate, ground by a wet process and dried, treated by means of 1% by weight of stearic acid, with resulting granulometry equal to 96% < 1 micrometre and 39% < 0.2 micrometres measured by means of the Sedigraph 5000 from the Micromeritics company, with specific surface, after treatment, equal to 28 m²/g measured according to the ISO standard 4652 B.E.T. method and with oil absorption, after treatment, equal to 19.5 measured according to ISO standard 787-V (Rub-out method).

PRODUCT G:

A rheology regulator according to the invention, consisting of a chalk type natural calcium carbonate, ground by a wet process and dried, untreated, with specific surface 22 m²/g measured according to the ISO standard 4652 B.E.T. method and with oil absorption equal to 19.4 measured according to ISO standard 787-V (Rub-out method).

PRODUCT H:

A filler of the prior art consisting of a precipitated calcium carbonate marketed by the Zeneca company under the name Winnofil SPTTM.

PRODUCT I:

A filler of the prior art, consisting of a chalk type natural calcium carbonate, ground by a wet process and dried, treated by means of 1% of stearic acid, with mean diameter equal to 1.4 micrometres measured by means of the Sedigraph 5100 from the Micromeritics company and with specific surface equal to 6 m²/g measured according to the ISO standard 4652 B.E.T. method.

PRODUCT J:

A filler of the prior art, consisting of a chalk type natural calcium carbonate, ground by a wet process and dried, treated by the use of 1% by weight of stearic acid, with mean diameter equal to 1 micrometre measured by means of the Sedigraph 5100 from the Micromeritics company and specific surface 10 m²/g measured according to the ISO standard 4652 B.E.T. method.



PRODUCT K:

A filler of the prior art consisting of a treated precipitated calcium carbonate marketed by the Solvay company under the name Socal U1S2.

5

EXAMPLE 1:

This example concerns the use of calcium carbonates as rheology regulators for the preparation of plastisois.

10

These tests tested the replacement of the synthetic calcium carbonate obtained by precipitation, of the prior art, or precipitated calcium carbonate (PCC) by the specific natural calcium carbonate according to the invention.

15

In a PVC (polyvinyl chloride) based plastisol formulation not containing calcium carbonate, it was sought to compare the effect of substituting 50% to 100% of the mineral filler usually used, namely a precipitated calcium carbonate, by an ultra-finely ground natural calcium carbonate according to the invention.

20

To do this, the calcium carbonate to be tested is mixed with 75 g of plastisol without filler in a 7cm-diameter container and homogenization is carried out with a spatula. The mixture is then dispersed for 2 minutes by means of a "Pendraulik"TM LD50 laboratory mixing apparatus, the diameter of the dispersing disk being 5 cm and the speed of rotation of the disk being 2700 rpm (manual setting in position 3).

25

The dispersing being finished, the viscosity is measured by means of the "Rheomat 120"TM apparatus, a measuring device according to DIN standard 125, at 20°C.

30 Test 1:

This test illustrates the prior art and uses 20 g of a precipitated calcium carbonate marketed by the Zeneca company under the name Winnofil SPTTM (product H) and 5 g of natural calcium carbonate sold under the name JuraperleTM BS by the Juraweiss company.

35

Test 2:

This test illustrates the prior art and uses 13 g of a precipitated calcium carbonate marketed by the Zeneca company under the name Winnofil SPTTM (product H) and 12 g of product A according to the invention.



Test 3:

This test illustrates the invention and uses 25 g of product B according to the invention.

5 Test 4:

This test illustrates the prior art and uses 20 g of a precipitated calcium carbonate marketed by the Zeneca company under the name Winnofil SPT™ (product H).

Test 5:

- 10 This test illustrates the invention and uses 10 g of a precipitated calcium carbonate marketed by the Zeneca company under the name Winnofil SPT™ (product H) and 15 g of product D according to the invention.

Test 6:

- 15 This test illustrates the invention and uses 10 g of a precipitated calcium carbonate marketed by the Zeneca company under the name Winnofil SPT™ (product H) and 15 g of product C according to the invention.

Test 7:

- 20 This test illustrates the invention and uses 13 g of a precipitated calcium carbonate marketed by the Zeneca company under the name Winnofil SPT™ (product H) and 12 g of product E according to the invention.

Test 8:

- 25 This test illustrates the invention and uses 10 g of a precipitated calcium carbonate marketed by the Zeneca company under the name Winnofil SPT™ (product H), 5 g of natural calcium carbonate sold under the name Juraperle™ BS by the Juraweiss company and 10 g of product D according to the invention.

30 Test 9:

This test illustrates the invention and uses 10 g of a precipitated calcium carbonate marketed by the Zeneca company under the name Winnofil SPT™ (product H), 5 g of natural calcium carbonate sold under the name Juraperle™ BS by the Juraweiss company and 10 g of product E according to the invention.

35

Test 10:

This test illustrates the invention and uses, for a mixture with 72 g of plastisol, 10 g of a precipitated calcium carbonate marketed by the Zeneca company under the name Winnofil SPT™ (product H), 5 g of natural calcium carbonate sold under the name



Juraperle™ BS by the Juraweiss company and 13 g of product E according to the invention.

The results of the viscosity measurements as a function of the flow rate according to DIN
5 standard 125 at 20°C are assembled in Tables Ia and Ib below.



TABLE Ia

C O M P O S I T I O N	TEST No.	Prior art	Prior art	Invention	Prior art	Invention
		1	2	3	4	5
	Plastisol without filler (in g)	75.00	75.00	75.00	75.00	75.00
	PCC (in g)	20.00	13.00	-	25.00	10.00
	Juraperle™ BS (in g)	5.00	-	-	-	-
	Product A (in g)	-	12.00	-	-	-
	Product B (in g)	-	-	25.00	-	-
	Product D (in g)	-	-	-	-	15.00
	Weight of the mixture (in g)	100.00	100.00	100.00	100.00	100.00



R H E O L O G Y	Viscosity mPa.s	Test No.	Test No.	Test No.	Test No.	Test No.
	Flow rate s ⁻¹	1	2	3	4	5
	20	18200	17700	15200	17600	17100
	40	10040	9650	8430	9900	9650
	60	7260	7100	6280	7200	7100
	80	5890	5730	5170	5850	5700
	100	5100	4880	4390	5000	4800
	120	4490	4380	3980	4450	4350
	140	4100	4020	3550	3990	3990
	160	3780	3650	3310	3650	3650
	180	3460	3400	3110	3400	3380
	200	3320	3220	2950	3190	3170
	220	3140	3030	2780	3110	3000
	240	3000	2870	2620	2890	2820
	260	2870	2760	2520	2740	2700
	280	2760	2680	2420	2610	2600
	300	2660	2570	2350	2490	2490



TABLE Ib

C O M P O S I T I O N	TEST No.	Invention	Invention	Invention	Invention	Invention
		6	7	8	9	10
	Plastisol without filler (in g)	75.00	75.00	75.00	75.00	72.00
	PCC (in g)	10.00	13.00	10.00	10.00	10.00
	Juraperle™BS (in g)	-	-	5.00	5.00	5.00
	Product C (in g)	15.00	-	-	-	-
	Product D (in g)	-	-	10.00	-	-
	Product E (in g)	-	12.00	-	10.00	13.00
	Weight of the mixture (in g)	100.00	100.00	100.00	100.00	100.00



R H E O L O G Y	Viscosity mPa.s	Test No.	Test No.	Test No.	Test No.	Test No.
	Flow rate s ⁻¹	6	7	8	9	10
	20	12700	17300	13100	12500	17000
	40	7280	9450	7600	7160	9500
	60	5360	6950	5630	5250	7030
	80	4430	5600	4850	4330	5580
	100	3820	4830	4040	3780	4800
	120	3400	4230	3600	3300	4320
	140	3110	3950	2290	3000	3790
	160	2860	3550	3040	2770	3550
	180	2680	3260	2850	2590	3280
	200	2520	3110	2680	2480	3080
	220	2400	2910	2550	2320	2950
	240	2290	2790	2430	2200	2800
	260	2190	2670	2340	2130	2710
	280	2120	2580	2250	2050	2610
	300	2040	2490	2180	1970	2490



A reading of the table makes it possible to see that use of the calcium carbonate according to the invention makes it possible to regulate the rheological behaviour of the plastisol composition, even when 100% of the precipitated calcium carbonate has been replaced by the calcium carbonate according to the invention.

EXAMPLE 2:

This example concerns the study of the conventional mechanical properties imparted by the product F according to the invention, that is a natural chalk ground so as to obtain a specific surface of $28 \text{ m}^2/\text{g}$, to plasticized PVC-based mixtures, in comparison with mixtures provided with filler by means of natural calcium carbonates well known to the prior art.

For each of the tests, the following mixture was produced:

"SOLVIC 239 D" PVC marketed by the Solvay company	100
Dioctyl phthalate (Jayflex™ DOP from Exxon)	50
Dibasic lead sulphate	1
Tribasic lead sulphate	2
Filler to be tested	80

Preparation of the composition:

The dry mixtures or dry blends are prepared with the "GUEDU"™ adiabatic mixer, at 100°C for a period of 15 minutes. The mixtures are then gelled on cylinders at 150°C with the cylinder kneader. For all the mixtures, this operation is performed in 12 minutes.

90 x 90 x 2 mm sheets are then moulded at 160°C after preheating of the blank for 3 minutes and placing under pressure for 2 minutes before cooling, by means of a compression press.

The test pieces necessary for determining the mechanical properties were cut out from these sheets.

The different calcium carbonates tested are:



Test 11:

This test illustrates the prior art and uses a natural chalk, treated with 1% of stearic acid, with specific surface 6 m²/g measured according to the ISO standard 4652 B.E.T. method (product I).

5

Test 12:

This test illustrates the prior art and uses a natural chalk, treated with 1% of stearic acid, with specific surface 10 m²/g measured according to the ISO standard 4652 B.E.T. method (product J).

10

Test 13:

This test illustrates the invention and uses product F according to the invention.

15

The mechanical properties are assessed by the dynamometric tests (breaking strength, elongation at breaking, 100% modulus) carried out by use of the Instron™ apparatus according to ISO standard 37, at a temperature of 23°C and for a strain rate of 10 cm/min.

20

The ASTM-C resistance to tearing is determined according to the method of ISO standard R-34 and the Shore C hardness according to the method of ISO standard 868.

The results of these mechanical property measurements are assembled in Table II below.

25

TABLE II

Test No.	Prior art	Prior art	Invention
	11	12	13
Breaking strength (daN/cm ²)	128	130	136
Elongation at breaking (%)	300	260	172
100% modulus (daN/cm ²)	83	106	127
ASTM-C resistance to tearing (daN/cm)	47	56	58
Shore C hardness at 15 s (in daN/cm)	60	64	74



It can be seen that the mechanical properties obtained are excellent and are superior to those obtained with ground natural calcium carbonates but with specific surface outside the field of the invention.

5

The invention therefore makes it possible to optimize the formulations according to the mechanical property to be given greater importance.

EXAMPLE 3:

10

This example concerns the use of calcium carbonates as rheology regulators for the preparation of natural and synthetic rubber-based elastomer.

15 An attempt has been made in this example to assess the influence of the specific surface of a ground natural chalk according to the invention on the properties of natural and synthetic rubber-based mixtures, in comparison with a precipitated calcium carbonate of the prior art.

To do this, for each of tests 14 and 15, the following mixture was produced:

20

Natural rubber (RSS 1 quality smoked sheet)	100
SBR rubber (styrene-butadiene, Cariflex™ 1502 from Shell)	40
Zinc oxide (snow quality) from Vieille Montagne	5
Stearic acid	2
25 Sulphur	1.5
N-cyclohexyl 2 benzothiazyl sulphenamide (Vulcafor™ CBS from Vulnax)	1
Tetramethyl-thiuram disulphide (Vulkacit™ DTMT from Bayer)	0.5
Calcium carbonate to be tested	100

30 Test 14:

This test illustrates the prior art and uses a precipitated calcium carbonate marketed by the Solvay company under the name Socal U1S2 (product K).

Test 15:

35

This test illustrates the invention and uses product F according to the invention.

These two test are carried out as follows:



A pure gum master batch is prepared, by successive incorporation of the various ingredients apart from the calcium carbonate according to the usual technique of persons skilled in the art, on a temperature-regulated cylinder kneader, by kneading for 10 minutes (friction 1/1.4) at 60°C.

5

From this master batch, two samples were taken, into which the calcium carbonates to be tested were incorporated, by kneading at 60°C for 12 minutes.

After determination of the vulcanization optimums at 155°C by means of the Monsanto rheometer, sheets were moulded and vulcanized at this optimum in order to measure the mechanical properties according to the same operating method as that of the previous tests.

10

The mechanical property results are assembled in Table III below.

15

TABLE III

Test No.	Prior art	Invention
	14	15
Vulcanization optimum at 155°C	5 min 15 sec	5 min
Breaking daN/cm ²	119	109
300% modulus daN/cm ²	41	39
Elongation %	500	485
ASTM-C tearing daN/cm	23	26
Shore A hardness (15 s)	61	61

It can be seen that the product according to the invention reduces the implementation time (vulcanization optimum) as well as the resistance to tearing properties.

20

Tests 16, 17 and 18 are carried out similarly by use of the following formulation:



	SBR rubber (styrene-butadiene, Cariflex™ 1502 from Shell)	40
	Natural rubber (RSS 1 quality smoked sheet)	60
	Zinc oxide (snow quality) from Vieille Montagne	5
5	Stearic acid	2
	Sulphur	2
	N-cyclohexyl 2 benzothiazyl sulphenamide (Vulcafor™ CBS from Vulnax)	0.9
	Diorthotolylguanidine accelerator (Vulcafor™ DOTG from Vulnax)	0.3
	Calcium carbonate to be tested	100

10

Test 16:

This test illustrates the prior art and uses a precipitated calcium carbonate marketed by the Solvay company under the name Socal U1S2 (product K).

15 Test 17:

This test illustrates the prior art and uses a chalk type calcium carbonate, ground by a wet process and dried, treated, with mean diameter equal to 1.4 micrometres measured by means of the Sedigraph 5100 from the Micromeritics company and with specific surface equal to 10 m²/g measured according to the ISO standard 4652 B.E.T. method

20 (product J).

Test 18:

This test illustrates the invention and uses product G according to the invention.

25 From this master batch made with the same operating method as in the previous test, three samples were taken, into which the calcium carbonates to be tested were incorporated, by kneading at 60°C for 12 minutes.

30 After determination of the vulcanization optimums, sheets were moulded and vulcanized at this optimum in order to measure the mechanical properties according to the same operating method as for the previous tests.

The mechanical property results are assembled in Table IV below.



TABLE IV

	Prior art	Prior art	Invention
Test No.	16	17	18
Vulcanization optimum at 150°C	23 min 30 sec	16 min 45 sec	11 min
Breaking strength (daN/cm ²)	122	132	132
300% modulus (daN/cm ²)	16.5	20	20
Elongation %	695	715	695
ASTM-C resistance to tearing (daN/cm)	23	28	28
Shore A hardness (15 s) in (daN/cm)	51	50	50

5

It can be seen that the product according to the invention improves the implementation time (vulcanization optimum) and the majority of the mechanical properties.

10 EXAMPLE 4:

A second series of tests (tests 19 and 20) were carried out in a natural rubber filled at 40% with mineral filler and with the basic formula:

15	Natural rubber (RSS 1 quality smoked sheet)	100
	Coumarone 60/70 resin	5.6
	Colophane resin	3
	Zinc oxide (snow quality) from Vieille Montagne	40
	Stearic acid	0.5
20	Oil	4.3
	Benzothiazyl disulphide accelerator (Vulcafor™ MBTS from Vulnax)	1
	Diphenylguanidine accelerator (Vulcafor™ DPG from Vulnax)	0.36

The calcium carbonates to be tested are:

25



Test 19:

A precipitated calcium carbonate (product K) for this test which illustrates the prior art.

Test 20:

- 5 A natural calcium carbonate according to the invention (product G) for this test which illustrates the invention.

The results for the mechanical properties, measured with the same operating method as for the following tests, are assembled in Table V below.

10

TABLE V

	Prior art	Invention
Test No.	19	20
Vulcanization optimum at 150°C	7 min 15 sec	8 min 15 sec
Breaking strength (daN/cm ²)	246	246
300% modulus (daN/cm ²)	32	31
Elongation %	710	710
Shore A hardness (15 s) in (daN/cm)	45	46.5

- 15 It can be seen that the product according to the invention makes it possible to obtain equivalent mechanical property results, even by replacing all the precipitated calcium carbonate by a natural calcium carbonate.



The claims defining the invention are as follows:

1. Use of a finely ground natural calcium carbonate having a specific surface area of approximately 14 to 30m²/g, which is measured according to the B.E.T. method ISO standard 4652, as a rheology controller.

5 2. The use of claim 1, wherein the specific surface area of the natural calcium carbonate is approximately 16 to 24m²/g.

3. The use of claim 1 or 2, wherein the specific surface area of the natural calcium carbonate is 20m²/g.

4. The use of claim 1, wherein the natural calcium carbonate has a specific surface area of 14.4m²/g.

5. The use of claim 1 or 2, wherein the natural calcium carbonate has a specific surface area of 16m²/g.

6. The use of claim 1 or 2, wherein the natural calcium carbonate has a specific surface area of 16.5m²/g.

15 7. The use of claim 1 or 2, wherein the natural calcium carbonate has a specific surface area of 22m²/g.

8. The use of claim 1, wherein the natural calcium carbonate has a specific surface area of 28m²/g.

9. The use according to any one of claims 1 to 8, wherein the natural calcium carbonate is treated by means of at least one fatty acid containing 10 to 24 carbon atoms or its salt chosen from amongst the salts of calcium, magnesium, zinc or a mixture thereof.

10. The use of claim 9, wherein the at least one fatty acid is stearic acid or its calcium salt.

25 11. The use of claim 10, wherein the stearic acid or its calcium salt is used in a proportion of approximately 0.01% to 5% by weight.

12. The use of any one of claims 9 to 11, wherein the natural calcium carbonate is stearic acid or its calcium salt used in a proportion of the order of 1% to 4% by weight.

30 13. The use according to any one of claims 1 to 12, wherein the natural calcium carbonate has an oil absorption which is higher than 16 which is measured according to ISO standard 787-V (Rub-out method).

14. The use according to any one of claims 1 to 13 for the preparation of mastics, adhesives or plastisols.



15. The use according to any one of claims 1 to 13 for the preparation of rubbers.

16. The use according to any one of claims 1 to 13 wherein the finely ground natural calcium carbonate is in a dispersion or suspension of an organic medium
5 for the preparation of mastics or coatings, adhesives or plastisols.

17. The use according to claim 15 wherein the finely ground natural calcium carbonate is in a dispersion or suspension of an organic medium.

18. Use of a finely ground natural calcium carbonate as a rheology controller substantially as hereinbefore described with reference to any one of the
10 examples.

19. A plastisol comprising a rheology controller as defined in any one of claims 1 to 13 or 18.

20. A rubber comprising a rheology controller as defined in any one of claims 1 to 13 or 18.

15 21. A mastic, coating or adhesive comprising a rheology controller as defined in any one of claims 1 to 13 or 18.

22. A mastic, coating or adhesive according to claim 21, wherein the mastic, coating or adhesive comprises in addition a polyurethane with terminal silane groups and a plasticizer of the phthalate type.

20 23. A mastic, coating or adhesive according to either claim 16 or 17, which comprises in addition one or more additives chosen from amongst smoked silica as a thixotropic agent, a whitening agent such as TiO_2 , UV stabilizers, agents promoting adhesion, catalysts such as dibutyltin dilaurate, and dehydrating agents such as silane.

Dated 8 January 2003

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